ACIDS AND BASES.[*]

BY

GILBERT N. LEWIS, Ph.D., D.Sc.,

Department of Chemistry, University of California, Berkeley, California.

In the last few years there has been a renewed interest in acids and bases and their nomenclature. Names are themselves of little consequence except in so far as they imply some systematic classification which may be of vital importance in the development of a science. Lavoisier, the greatest of all chemical systematists, used the word acid in a broad sense. Carbon dioxide was known as carbonic acid gas and sulfurous acid meant, as it still does in some languages, the anhydride SO_2. However, during the nineteenth century it became the fashion to regard hydrogen as an indispensable constituent of an acid, and finally the concept of acids and bases became so much restricted that in the minds of some of the early advocates of the ionic theory the only acid was an aqueous solution containing hydrogen ion, and the only base an aqueous solution containing hydroxide ion.

Such an idea could not be accepted by organic chemists, who recognized in ammonia and its derivatives substances which are bases in their own right, and not merely because they produce hydroxide ion when dissolved in water. So, also, the discovery of oxonium compounds led to further generalization and this process has continued up to the present.

It is possible, as I shall attempt to show in this paper, to discuss and define acids and bases merely from their behavior in chemical reactions without any theory of molecular structure. Nevertheless the development of the electronic views of valence made it easier to understand the essential characteristics of these two classes. In my book on "Valence," [1] after discussing various methods by which the idea of acids

---

[*] Presented Friday morning, May 20, 1938.

[1] "Valence and the Structure of Atoms and Molecules," Chemical Catalog Company, New York, 1923.

and bases could be extended, I proposed a very general definition of acids and bases. According to that definition, a basic molecule is one that has an electron-pair which may enter the valence shell of another atom to consummate the electron-pair bond; an acid molecule is one which is capable of receiving such an electron-pair into the shell of one of its atoms. Professor Sidgwick,[2] who has made such careful and extensive investigation of the consequences of our electronic conception of valence, calls the molecule which gives the electron-pair a *donor* molecule and the other an *acceptor* molecule. This expressive nomenclature I should be glad to adopt if I did not hope to show that his classification coincides absolutely with the classification of acids and bases, so that the need for new names disappears.

When the idea of the pairing of electrons was being first developed it was necessary to draw merely from the chemical behavior of substances some conclusions regarding electronic structure. Theoretical physics at that time offered no help except in so far as it had shown that the assumption of mere coulombic forces was incompatible with the existence of any stable atom or molecule composed of positive nuclei and electrons.   ·

More recently, and largely since I last wrote on this subject fifteen years ago, conditions have radically changed. On the one hand, the development of numerous precise methods of measurement has furnished very exact information regarding the shape and size of many molecules.[3] On the other hand, quantum mechanics has revolutionized our idea of the inter-actions of material particles, especially in systems of small size. It is interesting therefore to find that the conclusions which were based on purely chemical, and largely qualitative, observations have retained their validity, and in many cases have been strengthened by the newer knowledge.

The principle of Pauli gave the first physical interpretation of the pairing of electrons, and Heitler and London were able to deduce from quantum mechanics the electron-pair bond.

---

[2] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1929.

[3] See the interesting monograph by H. A. Stuart, "Molekülstruktur," J. Springer, Berlin, 1934.

It is true that the old idea of the exact localization of electrons in a molecule has had to be abandoned.   Instead we have the more nebulous "electron cloud."   However the denser part of this cloud, which represents the region in which the electron is by far the most likely to be, coincides, in the case of all compounds of the more nearly saturated type, with the electron positions demanded by chemical formulas.   In unsaturated molecules where the "electron cloud" is less definitely localized, we often find that the properties cannot be well represented by a single chemical formula.

While it finally proved possible to reconcile quantum mechanics with the chemical requirement of the complete symmetry of the four bonds of methane, there is one chemical demand which the development of quantum mechanics has not as yet satisfied.   It was an essential element in the original theory of the octet, not only that an atom bonded to four others would have the electron-pairs in tetrahedral positions, but that this would still be true even if one or two of the electron-pairs were not used in bonds.   From this it was deduced that water would not have a linear structure nor ammonia a planar structure, and that the position of a non-bonding pair would be so situated at a corner of a tetrahedron as to produce optical isomerism, such as has been actually found in sulfonium compounds.   Even to the simplest molecule the application of quantum mechanics is too difficult for anything more than approximate treatment.   However, if an exact treatment ever becomes possible, we may be sure that it will show in the case of a molecule such as that of ammonia not only the concentration of "electron cloud" representing each of the bonds to the three hydrogen atoms, but also a fourth concentration in the form of a protuberance in the fourth tetrahedral position, and that this projection due to the unbonded electron-pair is the entity which is characteristic of basic molecules.

It is always of interest to find that some of our most modern scientific ideas have been vaguely anticipated by scientists of earlier centuries.   One of the ideas of Lémery, a contemporary of Robert Boyle, is amusingly discussed in a well known history of chemistry, as follows: [4] "Yet one of his

---

[4] James Campbell Brown, "History of Chemistry," 1913.

theoretical conceptions was very odd, and shows how far astray a capable man may wander, when he deserts observed facts for philosophical speculations. He thought that chemical combination between two substances, such as an acid and a base, might be accounted for by supposing that the particles of the one substance were sharp, and those of the other porous, and that combination was effected by the *fitting of the points into the holes!*"

Before proceeding to defend my general definition of acids and bases, I may say a word concerning an even more general notion which has occasionally been suggested, namely, that an acid molecule is merely one in which there is some region which is electrically positive, that a basic molecule is one which in some part has an excess of negative electricity, and that the process of neutralization is the drawing together of the positive part of the one molecule and the negative part of the other through coulombic forces. Indeed, it has been found in many cases that it is possible to calculate, with good approximation, the heat of formation of a compound by this simple and old-fashioned expedient. This is due to the fact that Coulomb's law is nearly valid from large distances down to the immediate neighborhood of the molecule. However, in this neighborhood it is necessary to replace that law by the new principles of quantum mechanics, and it is in this neighborhood that occur most of the phenomena which are of particular interest to chemists. It is by no means possible by coulombic considerations to understand the limiting of carbon and its neighbors to a valence of four. When we consider the valence, or coördination number, of heavier elements, the coulombic view correctly predicts that the coördination number of a metallic ion will be larger the greater the positive charge on the ion, but it could in no way predict that these coördination numbers are almost always even; nor could it predict that in a coördination zone neutral molecules can be replaced by singly charged ions or by doubly charged ions without affecting the essential properties of the molecule.

Since the coulombic method often leads to approximately correct results, it is not surprising to find that, as H^+ is our type acid, so most anions have definite basic properties. Yet an ion like ClO_4^- is hardly a base at all, and while, in our

generalized system of acids, most positive ions are definitely acidic, such an ion as NR_4^+ cannot be regarded as an acid in any sense whatever. It is partly because the ions as acids and bases have been somewhat over-emphasized that we shall deal largely in this paper with acids and bases composed of neutral molecules.

The recognition by Brönsted and his school of such ions as the halide ions and acetate ion as true bases, together with the development of the concept of organic bases, tends to make the present recognized list of bases identical with my own. On the other hand, any similar valuable and instructive extension of the idea of acids has been prevented by what I am tempted to call the modern cult of the proton. To restrict the group of acids to those substances which contain hydrogen interferes as seriously with the systematic understanding of chemistry as would the restriction of the term oxidizing agent to substances containing oxygen. It is true that the term acid comprises at present not only hydrogen ion [5] but also undissociated acids, and correctly so, since H^+, owing to the phenomenon known as the formation of the hydrogen bond, is a dibasic acid. If, for example, it combines with the base OH^-, it can further combine with the base NH_3 to form the undissociated molecule NH_4OH. How does this behavior differ essentially from that of silver ion to which we ascribe the usual coördination number of two? Ag^+ can first combine with the base OH^-, and later with the second base NH_3, forming the molecule NH_3AgOH. Of course it might be supposed that hydrogen, because of its high mobility or its unique place in the periodic table, might give to hydrogen acids, or, as we may call them for short, H-acids, properties which distinguish them greatly from other acid substances, but as we proceed we shall find instead an astonishing similarity between H-acids and all the other members of the general acid group.

---

[5] I realize that it is unfashionable to speak of hydrogen ion. It was a familiar idea, even in the latter years of the nineteenth century, that hydrogen ion in water is largely hydrated. There must be several molecular species in solution such as H^+, H_3O^+, $H_5O_2^+$. If we wish to refer specifically to one of these, such as hydronium ion, H_3O^+, we may, but it seems best to keep the name hydrogen ion, and to use the symbol H^+ as shorthand designations for the whole group.

Before proceeding to a detailed consideration of the criteria of acids and bases, we may take provisionally as bases all those substances which, like hydroxide ion, "neutralize" hydrogen ion or any of the other members of our group of acids; and we may take as acids any of the substances which "neutralize" hydroxide ion or any of our other bases. We thus find that there is only a small number of elements whose atoms can contribute basic properties to a molecule. These are confined to the nitrogen, oxygen and fluorine families, occasionally carbon, and in one reported case a rare gas.[6] Choosing for our present purpose non-ionic bases which contain neither hydroxide nor labile hydrogen, we may take as examples of generalized bases *triethylamine, pyridine, acetone* and *ether.* These can be said to be arranged in the order of decreasing basic strength, but this is a question which we must later consider more carefully.

On the other hand, nearly all of the elements can act as acids; the only exceptions are the rare gases and probably the heavier members of the alkali and alkaline earth metals.[7] Choosing from the vast number of acids at our disposal, we will mention, for illustration, *sulfur trioxide, boron trichloride, stannic chloride, silver perchlorate, sulfur dioxide,* and *carbon dioxide.* These are arranged roughly in the order of diminishing acid strength. The acid properties of boron are due to

---

[6] Booth and Wilson (*J. Am. Chem. Soc.*, **57**, 2273 (1937)) have obtained, from a study of freezing points, evidence of the existence of compounds between argon and boron trifluoride. They suggest that more stable compounds could be obtained with krypton and xenon. Since sulfur trioxide is a considerably stronger acid than boron trifluoride toward most bases, it may be found to give even more stable compounds with the rare gases.

[7] There can be no question that lithium ion and beryllium ion act as true acids and attach themselves, forming bonds of considerable strength, to basic electron-pairs situated on a typical anion such as Cl⁻. As we proceed to the higher members of these two families, the strengths of such bonds become smaller until, in the case of cesium, it is doubtful whether in the gaseous state, or in solution in some solvent of low dielectric constant, the cesium ion is attached to a definite electron-pair on the anion. Instead we may consider cation and anion held together by purely coulombic forces and behaving essentially like two oppositely charged spheres. Such a molecule would frequently be said to possess a "polar bond," but personally I prefer to restrict the word "bond" to the cases in which two atoms are held together by an electron-pair, or, in the extremely rare type of the hydrogen molecule ion, by a single electron.

its tendency to complete its octet, or the stable group of four electron-pairs, those of tin and silver to the tendency to complete the stable groups of six and two electron-pairs, respectively.   Whether we speak of valence or coördination number, we must recognize that in all cases the phenomenon is the same.   The neutralization of an acid always consists in completing the stable number of electron-pairs which is characteristic of the atom to which the acid properties are due.

The stronger acids combine with the stronger bases to form stable compounds, while the weaker acids do not usually form compounds with the weaker bases.   Such rough statements regarding the relative strengths of acids and bases are useful, but are nevertheless likely to be misleading. In studying the phenomenon of oxidation and reduction it is convenient to say that zinc is a stronger reducing agent than copper, but in the Daniel cell the direction of the current can be reversed when a little cyanide is introduced at the copper electrode.   So in studying acids and bases we find that the relative strength depends not only upon the chosen solvent but also upon the particular base or acid used for reference. Thus in aqueous solution silver ion has little tendency to combine with hydroxide ion, and therefore with respect to this base we say that silver ion is a weak acid, but if a little ammonia is added to the solution, silver ion acts toward this new base as an acid comparable in strength with hydrogen ion of similar concentration.   In general when metallic salts, or other compounds belonging to our set of acids, are dissolved in water, we often estimate their relative strengths as acids by the concentration of hydrogen ion which they set free, but we are only determining the strength of the acid towards the particular base OH^-, in the particular solvent water.

I may cite at this point several cases of specific action between certain acids and certain bases, all of which are observable in aqueous solutions, and which show how impossible it is to arrange our acids in any single monotonic order.   Many heavy metallic ions, like silver ion, are relatively much stronger acids toward ammonia than toward water or OH^-. SO_2 is a weak acid and I^- and SCN^- are weak bases, but both these anions form fairly stable complexes

with SO_2 in aqueous solution, as can be noticed by the yellow color these complexes impart to the solution. The molecule $B(OH)_3$ can act as an acid (1) by giving off one or more hydrogen ions, (2) as a typical H-acid through the formation of the hydrogen bond, and (3) by giving boron its fourth bond, and thus completing its octet. This last type of acid behavior, which is shown very clearly by the ability of the ester $B(OR)_3$ to act as an acid,[8] is especially evident in the ability of boric acid to displace hydrogen from a simple alcohol to form the simple B-O-C linkage, and becomes extremely pronounced whenever the organic molecule has two basic atoms so situated that they can both combine with a single boron atom to form a five or six membered ring. This phenomenon is not restricted to boron alone but is a property of many elements, and we shall have occasion later to mention the remarkable behavior of gallium.

In a rough way we can understand and sometimes predict this specificity of action between acids and bases, partly from a consideration of atomic volume and polarizability, partly from properties of rings, and partly through a study of mesomerism or resonance,[9] but for any exact formulation far more data are necessary than are now available.

Aqueous solutions afford but a small range of acid and basic strength. A really strong acid like sulfur trioxide or a really strong base like sodium nitride are almost completely hydrolyzed in water. This phenomenon, which has been called by Hantsch the "leveling effect," occurs in two stages. Since water is both an acid and a base it combines directly with any strong base or acid, and in addition hydroxide ion or hydrogen ion is set free. Just as in considering the problem of oxidation and reduction we find that we can have in water no rapid reducing agents stronger than H_2 nor any rapid oxidizing agents stronger than O_2, so in water we

---

[8] $B(OR)_3$ forms compounds with alkalies and also with alcoholates (Copaux, *Comp. Rend.*, **127**, 721 (1898)). The boron is acting here just as it does in the widely different class of compounds between boron trialkyls and ammonia or amines.

[9] For an introduction to the idea of resonance, an idea which is becoming increasingly important in chemistry, and to which we shall have frequent occasion to refer, see Pauling's Chapter 22 in Gilman's "Organic Chemistry," John Wiley and Sons, 1938.

can have no acid stronger than H^+ and no base stronger than OH^-, except for such specific effects as have been mentioned.

Many solvents are *amphoteric* in the sense that they may serve both as acids and bases. Their molecules can therefore combine with one another and thus we explain the high degree of association in such liquids as water and alcohol, or ammonia and the primary and secondary amines. Such association disappears in the case of ethers and trialkylamines, which act only as bases.

This amphoteric character is possessed by many of our generalized strong acids. The oxygen in sulfur trioxide has extremely weak basic properties, but SO_3 is so powerful an acid that it is able to attach itself to the oxygen of another molecule, thus forming the double or continuing molecules characteristic of this class of substances. So also aluminum or ferric halides are amphoteric and when dissolved in an inert solution form double molecules, but in a solution even so weakly basic as ether they split into single molecules, which are now attached to the solvent rather than to each other.

Whenever two neutral molecules, one of which is an acid and the other a base, combine with one another, a condition of electric stress is produced, owing to the fact that the electron-pair which formerly belonged to the base alone is now shared by the two molecules. Thus a high dipole moment is set up unless it can be relieved by some molecular rearrangement. Thus when a molecule of carbon dioxide combines with a molecule of ammonia, no stable molecule would be formed were it not for the simultaneous transfer of one atom of hydrogen from nitrogen to oxygen, thus producing a molecule of carbamic acid, and relieving the electric tension.

In the acids and bases listed above, where such rearrangement is impossible, we find no compounds between the weaker acids and the weaker bases. Nevertheless, using the stronger acids or bases, an enormous number of such compounds may be formed, possessing very simple formulas in terms of electron-pair bonds. However, few of these have been described, and still fewer have been named. They are the outcasts of our present chemical system. I may call

them pseudo-salts,[10] for although incapable of ionization, they will probably be found, especially in solvents of low dielectric constant, to have properties analogous to those of an inner salt or of a true salt dissolved in the same kind of medium.[11]

THE PHENOMENOLOGICAL CRITERIA OF ACIDS AND BASES.

Since it may seem objectionable to define such important terms as acids and bases by means of our still somewhat hypothetical structures involving electron-pairs, let us attempt to ascertain from chemical behavior alone what characteristics we will ascribe to these two great classes of substances. The following traits seem to be most important.

I. When an acid and a base can combine, the process of combination, or neutralization, is a rapid one.

II. An acid or base will replace a weaker acid or base from its compounds.

III. Acids and bases may be titrated against one another by the use of substances, usually colored, known as indicators.

IV. Both acids and bases play an extremely important part in promoting chemical processes through their action as catalysts.

It will be our task to examine with respect to these criteria our generalized acids and bases and to point out the similarity, and indeed the nearly complete identity between the behavior

---

[10] These pseudo-salts are of the same type as amine oxide, which, indeed, falls into this class if we consider it made up of the base, trialkylamine, and the acid, atomic oxygen.

[11] Pfeiffer ("Organische Molekülverbindungen," 2nd ed., Ferdinand Enke, Stuttgart, 1927) has made a very extensive and valuable collection of the literature pertaining to compounds between organic substances and metallic salts. He shows in numerous cases the great resemblances between these and the compounds of the same organic substances with H-acids. Unfortunately, as far as I know, there has been no similar attempt to bring together the facts concerning the similar and equally important compounds between organic substances and our other generalized acids such as the oxides of sulfur and the halides of boron. Pfeiffer draws many of his conclusions from the existence and composition of solid compounds. It seems to me however that, on account of the special laws governing close-packing and stability in crystals, our ideas of molecular structure must be obtained chiefly from molecules which can be proved to exist in the gaseous or dissolved state. It remains to point out that the substances which Pfeiffer and others call *molecular compounds* are produced by the union of an acid and a base, and that the bond joining them is no different from any of the other bonds with which chemists are familiar.

of these substances and the more restricted acids and bases of common usage.

In water an acid and base neutralize one another with extreme rapidity, and also in alcohol at all temperatures down to the freezing point of this solvent. As far as I am able to observe it is true also for our whole system of generalized acids and bases. I am inclined therefore to suggest the thesis that all molecules whose electronic formulas conform to my generalized definition of acids and bases combine without impediment. In other words, that the neutralization of a primary acid and base requires no heat of activation. This behavior is the more striking in that there is only one other type of chemical reaction which can occur without activation. That is the union of an odd molecule with an odd molecule. (We need not consider here the rare case mentioned in a preceding footnote in which two molecules of opposite charge are drawn and held together by purely coulombic forces.)

Frequently the simple formula does not represent the actual state of the molecules. Sometimes, as we have seen in the discussion of amphoteric substances, the molecules partly, or even wholly, neutralize one another. More often they are neutralized by the solvent in which they are placed. They may then be said to be secondary acids or bases. For example, the base B may be dissolved in the weak acid A, and completely neutralized, in the sense that all its basic electron-pairs are now used in bond formation. If now we add another stronger acid A', the process,

$$A' + AB = A'B + A,$$
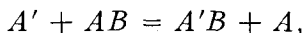
will ordinarily require activation, but the heat of activation should not be greater than the heat of formation of the compound AB. If this heat of formation does not amount to more than a few thousand calories, it is not easy to detect, and may for many purposes be ignored.

A far more interesting type of secondary acids and bases consists of those which are not acids or bases in their normal state of lowest energy, but become so through some internal excitation. Such an excitation may consist in the breaking of an existing bond. A typical case is furnished by carbon dioxide which, if represented with the double bond between

the carbon and each oxygen, or if represented by the other formulas which Pauling believes to resonate with this, always has four bonds attached to the carbon, which is therefore not acidic. In some of its excited states, however, one of these bonds may be broken. In fact it is found, experimentally, that the neutralization of carbon dioxide is a measurably slow reaction and would probably become very slow at low temperatures. Other secondary acids of the same type are substances like the organic acid chlorides and anhydrides. There is some reason for believing that sulfur dioxide also is only a secondary acid. It is stated that sulfur dioxide and ammonia do not combine as gases except in the presence of water vapor. We must be cautious in drawing such a conclusion, for in the gaseous state a reaction may fail to occur because it requires, not activation, but deactivation (as by a third body).

A substance which is neither acid nor base may become amphoteric in excited states. Thus a compound containing a double bond of the ethylene type may, when furnished sufficient energy, break a bond so that the electron-pair leaves one of the carbon atoms and belongs solely to the other. The former atom has now become a primary acid, the latter atom a primary base. This amphoteric character results often in polymerization.

Turning now to the second criterion, namely, the replacement of a weaker acid or base by a stronger one, we find just the same phenomena occurring with our generalized acids and bases as are familiar in aqueous solution, thus sodium carbonate in the presence of an aqueous acid evolves carbon dioxide. When we turn to solvents which contain no labile hydrogen the reaction is slower, owing to the small solubility of the carbonate, but I find, for example, that when finely divided Na_2CO_3 is warmed with BCl_3 or $SnCl_4$, in a mixture of equal parts of carbon tetrachloride and acetone, the carbon dioxide is soon evolved, leaving a compound which in the former case is insoluble, in the latter case soluble in the solvent. We shall find numerous examples of such replacement in our experiments with indicators, and sometimes a number of successive replacements can be shown. For example, boron trichloride, freshly dissolved in acetone, is neutralized by this

weakly basic solvent. If now a basic dye is added, this will replace the acetone, and finally a still stronger base like pyridine or a tertiary amine drives out the dye and forms its own compound with the boron trichloride.

EXPERIMENTS WITH INDICATORS.

Many chemists have carried out titrations of acids and bases with indicators in non-aqueous solvents, but they have used H-acids and usually solvents containing labile hydrogen. I have therefore carried out a large number of experiments, mostly of a qualitative character, with other members of the generalized group of acids, and in solvents whose constitution does not permit the formation of hydrogen ion or H-acids. (This is perhaps not quite true of one of the solvents employed, acetone, which has a small tendency to assume an enolic form.) I hoped by these experiments to show the changes in indicator color to be as sharp and the titrations as precise as in corresponding neutralizations in water. I was, however, unprepared for the really astonishing resemblances between the effects produced by the H-acids and the other more generalized acids. I venture to say that any one who has carried out for himself a few of these titrations will never again think of acids in the present restricted way.

I cannot describe here all these experiments, but a few of them may be summarized. First a variety of indicators were dissolved in dioxane and acetone. As bases, pyridine and triethylamine were used, and as acids, sulfur dioxide, solutions of boron trichloride and of stannic chloride in carbon tetrachloride, and silver perchlorate dissolved in benzene. The colors observed are different in different solvents. However, with one solvent and one indicator, the colors obtained seem to be dependent only upon the acid or basic condition of the solution and not at all upon the particular acid or base. The only exceptions are that with some indicators sulfur dioxide proves to be too weak an acid to give the acid color, and that sometimes one of the acids forms an insoluble precipitate [12] with the indicator, which, however, redissolves with excess of base. By means of the color changes the solutions can be

---

[12] Insoluble compounds between dyes and metallic salts, known as lakes, have been known and used for centuries in the dye industry.

titrated back and forth as readily as in aqueous solution. As an example, we may consider thymol blue dissolved in acetone. With both bases the color is yellow, while the acids, $AgClO_4$, SO_2, $SnCl_4$ and BCl_3, give an apparently identical bright red color.

The same red color was also obtained by HCl and this, together with the fact that none of the reagents had been especially dried, gave rise to the suspicion that some of the astonishing similarities [13] in color produced by the different acids were due to the existence of small impurities of H-acids in the reagents. For this reason the experiments were continued with a series of very dry solvents, which were kindly placed at my disposal by Dr. C. H. Li, with indicators which themselves contain no labile hydrogen, such as butter yellow, cyanin, and crystal violet. Finally a number of experiments were performed upon the vacuum bench with the assistance of Dr. G. T. Seaborg, whom I wish to thank for valuable help in these and other experiments. Such precautions were taken as to reduce the water and H-acids in the system to amounts negligible even compared with the small amount of indicator used. Nevertheless, these experiments gave results identical with those of the previous series.

Butter yellow, which is yellow in dry toluene, turns red when a minute amount of stannic chloride is added, and this is followed by the formation of a red precipitate. Upon the addition of a small amount of triethylamine the precipitate is dissolved and the original yellow color is restored. Sulfur dioxide behaves as a much weaker acid. When it is gradually added to the solution of butter yellow in toluene the solution

---

[13] I would have been less surprised by the identical colors produced by the several acids if I had known of the work done thirty years ago by K. H. Meyer (*Berichte deut. chem. Ges.*, **41**, 2568 (1908)). Meyer showed that the color of fuchson is the same in chloroform containing stannic chloride as in concentrated sulfuric acid. Not only is the visual color the same, but spectroscopic measurements of light absorption gave almost identical curves in the two cases. The same result was also obtained with benzaurin in the same two solutions. Meyer concluded that a molecule of stannic chloride, added to an indicator, gives a molecule which is extremely similar to one between the indicator and an H-acid. This conclusion could hardly be justified by this experiment alone, since in concentrated sulfuric acid the brilliant colors obtained with many dyes are probably due to compounds with partly dehydrated sulfuric acid, or even with SO_3.

becomes more and more red, but the full red color which would correspond to the complete neutralization of the indicator was not obtained even when the partial pressure of the sulfur dioxide reached one atmosphere.

Crystal violet is an indicator which exhibits the same colors in water and in many widely different solvents. In water, as the concentration of acid increases, the color changes from violet to green and then to yellow. It was shown in this laboratory by Rosenstein and Adams [14] that each change is due to the formation of a new substance as H^+ is added successively to the $N(CH_3)_2$ groups. When crystal violet dissolves in dry chlorobenzene it shows its characteristic violet color. With gradual addition of stannic chloride it passes through a green and then becomes yellow, after which the original violet color may be restored by an excess of triethylamine. Unless the acid is added carefully it is easy to pass through the green phase without observing it. If a similar phenomenon appeared in water we should say that the green solution exists only in a very small range of pH!

In the case of crystal violet it is not difficult to understand why the same colors are produced by different acids. In the original ion, which has an $N(CH_3)_2$ group in the para position of each benzene ring, there is resonance throughout the system of three identical rings. When one of the nitrogens, however, is neutralized by any acid, that ring is largely removed from the resonance system and we have the same conditions as in the green dye known as malachite green, which has only two para $N(CH_3)_2$ groups. When a second nitrogen is neutralized, either by H^+ or any other acid, only one ring is left in which the main resonance occurs.

Numerous indicators may be used in such solvents as we have employed that cannot be used in solvents like water. Thus triphenylmethyl chloride dissolved in chlorobenzene gives with BCl_3, $SnCl_4$, and $AgClO_4$ the bright yellow color characteristic of the triphenylmethyl cation. All that each acid does is to remove Cl^- from the indicator. In the last case silver chloride is precipitated and the color is due to the highly ionized triphenylmethyl perchlorate.

[14] Rosenstein and Adams, *J. Am. Chem. Soc.*, **36**, 1452 (1914).

Work with uncommon solvents possesses not only an intrinsic interest, but often enables us to obtain a clearer understanding of aqueous solutions themselves. If an indicator is dissolved in water and the solution contains no other important acids and bases than those derived from the indicator and from the water, we may expect to find a simple monotonic relation between the color and the pH of the solution. This is what is usually assumed to be true in all cases, even in the presence of other substances which I call acids and bases. However, as soon as we become acquainted with the high specificity in the mutual action of acids and bases, we can hardly expect to find so simple a behavior. In fact, as soon as we begin to look for cases in which the pH cannot be determined directly from the color, we find them on every hand. Turmeric turns brown in the presence of borate ion and this used to be an important method of qualitative analysis. Likewise alizarin and numerous other indicators which have two basic points, so situated that they can be attached to boron to form a five or six membered ring, behave towards boric acid and borates in the same way. It is interesting to note that while in most cases various acids give the same color to a dye, this does not seem to be true if an acid forms a ring compound with the indicator. The ring undoubtedly offers new opportunities for resonance, so that sometimes the color of the ring compound is nearer to that produced by a base than it is to the color produced by an ordinary acid.

Sulfide ion, like iodide ion, acts as a strong base toward some acids. For this reason I expected to find that the color of phenolphthalein would disappear on the addition of sulfide ion. This proved to be the case. The decolorization is not instantaneous and is entirely analogous to that produced by OH^- alone at high concentration. A more interesting case of similar type has been studied by Bouchard,[15] who found that the fluorescence of fluorescein, although not greatly affected by most ions, is much diminished by I^-, and to an even greater degree by S^{--}. It is evident that a person using this indicator and unaware of these facts might make serious errors in determining the acidity of solutions.

I have found numerous cases in which the ordinary rules

---

[15] Bouchard, *Comp. Rend.*, **196**, 485 (1933).

for determining pH from indicator colors fail completely.   I
shall mention only one, which is very striking.   Purpurin, in
aqueous acid solutions, has a yellow color which changes
through orange to a pink color at pH = 8.   If, however, in
acid solutions gallium chloride is added, even at so low a
concentration as 0.00001 M, the indicator gives the pink color
characteristic of alkaline solutions.   In a solution containing
a minute trace of gallium, a person using this indicator might
make an error of five units in pH.   The gallium ion seems to
combine even in these dilute solutions almost quantitatively
with the indicator, and probably in the ratio of three molecules
of dye to one gallium.   The gallium, acting as a strong acid,
nevertheless, because it forms a six membered ring, gives a
color aping that of a basic solution.   The indicator in basic
solution goes over to a more highly resonating form.   The
depression of this resonance by acid appears to be com-
pensated in part by the additional resonance of the new ring.

   Acid and Basic Radicals.   Before leaving the subject of
organic dyes, in which the optical and chemical properties
are known to be markedly influenced by substitutions in the
molecule, I wish to call attention briefly to an obvious and
indeed necessary extension of the idea of acids and bases.   We
have dealt heretofore with cases in which one molecule, an
acid, combines with another molecule, a base; but the same
sort of neutralization may occur within a molecule.   We are
thus led to the idea of acid and basic radicals.   Any substitu-
tion in a benzene ring may produce changes in the existing
resonance of the system, but there are certain groups which
have enormous effect because they are able to add new types
of resonance.   These are groups which can share an unbonded
electron-pair with a neighboring atom and are therefore basic
groups, and those which can share an electron-pair possessed
by a neighboring atom and are therefore acid groups.   These
two classes correspond entirely to the ortho-para orienting
groups and the meta orienting groups.   They also corre-
spond entirely to the auxochromes and anti-auxochromes of
Wizinger.[16]   The radicals NR_2 and NO_2 typify these two

[16] Wizinger, "Organische Farbstoffe," Ferd. Dümmlers, Berlin and Bonn,
1933.   I have found this book a very interesting and useful description of the
state of color chemistry up to the time when the idea of resonance was introduced.

classes. The former may form a double bond with an adjacent carbon atom and furnishes the necessary electron-pair. The latter may also form a double bond with an adjacent carbon atom, but the electron-pair must come from the rest of the molecule. Even though such a double bond is not wholly formed, in the sense of older structural formulas, its formation may constitute one member of a group of structures which are said to resonate with one another, and thus profoundly influences the character of the molecule.

Secondary Acids and Resonance in the Triphenylmethyl Group. Triphenylmethyl chloride in inert solvents is partly ionized, and this ionization is greatly favored by the substitution of $N(CH_3)_2$, so that crystal violet, which has one of these groups in each para position, behaves as a typical strong salt in aqueous solution. The ion is amphoteric in that it may act as a primary base and as a secondary acid. In the presence of acid, hydrogen ion adds instantly to the basic nitrogen until equilibrium is established. On the other hand, the addition of hydroxide ion to the central carbon, which is the process that causes bleaching in strong alkali, is slow and requires, according to the measurements of Biddle and Porter,[17] an activation energy of 14,000 calories. An entirely similar process occurs in the bleaching of phenolphthalein by OH^- and S^{--}, which we have just discussed.

Wizinger states that triphenylmethyl chloride, which dissolves in chlorobenzene to give a pale yellow solution, turns a bright yellow, owing to ionization, when heated to the boiling point of the solvent, and that it returns to its original color on cooling. I have repeated this experiment and find that when the boiling solution is cooled it does not return at once to the original pale color. In fact, if the boiling solution is rapidly chilled, it may be kept for hours at the temperature of ice, without appreciable loss of color. All these facts show that the plain and substituted triphenylmethyl cations are, not primary, but secondary acids.

In the formulation given by Pauling for the possibility of "resonance between two or more Lewis formulas," he shows that it is not only necessary that the energies of the several forms be nearly alike in order to make the resonance signifi-

---

[17] Biddle and Porter, *J. Am. Chem. Soc.*, **37**, 1571 (1915).

cant, but also that the several formulas must belong to what may be called the same quantum type.[18]   However it is evident that in complex molecules the question as to whether two formulas belong to the same type can hardly be settled by the few rules which have satisfactorily interpreted simple atomic spectroscopy.   Instead it may be necessary for some time to obtain such information empirically from observations of chemical behavior.

It seems obvious that resonance could not occur between a paramagnetic and a diamagnetic form.   It seems also unlikely that resonance can exist between two formulas, one of which contains odd electrons and the other only paired electrons.   Thus it seems to me that the one-electron bond formulas for B_2H_6, discussed by Sidgwick and by Pauling, cannot be included in the resonance system characteristic of this substance in its normal state.   What further restrictions are to be placed upon the kind of structures which may resonate with one another?   I should like to suggest tentatively, and as a subject of further investigation, that, at least in the triphenylmethyl series, there is no resonance between the formulas corresponding to a primary acid and those corresponding to a secondary acid.

If we consider the triphenylmethyl cation and its various derivatives we formerly had to choose between formulas which could be indicated by

$$- \overset{|}{C} - \text{ (I)} \quad\text{and}\quad - \overset{|}{C} = \text{(II)},$$
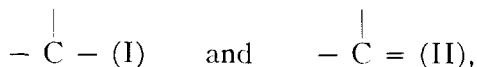
where I shows trivalent carbon and the positive charge situated in the neighborhood of this central carbon, while II shows a quinoid form with the positive charge transferred to some other part of the molecule.   In terms of present theory, I represents a group of resonance terms, while II represents a much larger group, for the double bond may belong to any one of the three rings and in that ring both ortho and para quinoid formulas are possible.   Now my contention is that there is no resonance at all between the formulas of group I and the formulas of group II, and that the resonating system II must suffer an excitation before it can go over to the system I.

---

[18] Pauling, *J. Am. Chem. Soc.*, **54**, 988 (1932).

A further experimental study of reaction velocities in such systems will be interesting.

ACIDS AND BASES AS CATALYSTS.

It has been pointed out that in aqueous solutions we can study only a small part of the range of acid and basic strengths. So we find that in water, while acids and bases show pronounced catalytic effects, they usually only accelerate reactions which occur to some extent without catalysis. When we turn to the stronger acids of our generalized system we find that they are capable of producing a great number of reactions which could not conceivably occur without their intervention. When we consider the various organic syntheses that are caused by strong acids such as the halides of many metals and of boron, we see more fully the scope of catalytic action. It is true that in many cases the substance which promotes the reaction is used up during its course, but there are many cases in which these substances act as true catalysts.

In this vast field almost no quantitative measurements of reaction velocities have been made, but some qualitative observations are pertinent to our purpose. We have seen that I^- and SCN^- act as strong bases towards SO_2. It is interesting therefore to recall some observations of Rosenheim.[19] He found that sulfur dioxide reacts with sodium ethylate in alcohol solution to give the ion $ROSO_2^-$, which can then go over to the sulfonate ion, RSO_3^-. This reaction is specifically catalyzed by I^- and CNS^-. This is evidently a clear case of basic catalysis, due to the formation of temporary intermediates between $ROSO_2^-$ and the basic ions.

When we turn to the consideration of aqueous solutions we may expect to find many similar instances of large specific catalytic action by various acids and bases. Such a phenomenon has not yet been found. It has long been accepted that reactions are promoted by hydrogen ion and by undissociated H-acids, and that the effectiveness of H-acids toward all reactions is a simple monotonic function of their acid strengths. This conclusion has seemed to be confirmed by a great deal of careful work on the part of Brönsted and his associates. Yet

---

[19] Rosenheim, *Berichte deut. chem. Ges.*, **31**, 405 (1898) and **38**, 1303 (1905).

from the ideas developed in this paper we must judge such a conclusion to be entirely erroneous.   The reason that specific strong catalysis by certain acids and bases has not been observed is not far to seek.   If we look at the reactions summarized by Schwab [20] we see that all the reactions which have been studied and used in support of the monotonic hypothesis have been reactions that involve hydrolysis, the addition of water to a molecule, the subtraction of water from a molecule, or the transfer of labile hydrogen from one part of the molecule to another.   As soon as reactions of a quite different type have been carefully studied in water and in other solvents, we may look for wide departures from the rule that acids and bases can be arranged in a definite order with respect to strength.

[20] Schwab, "Catalysis."   English translation by Taylor and Spence.   Van Nostrand, New York, 1937.